OPTICAL AND ELECTRICAL ENERGY GAPS IN
AMORPHOUS SEMICONDUCTORS*

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The experiments are analyzed which yield information about the density of localized gap states $g_L(E)$ in amorphous semiconductors. A conflict is found between optical absorption data which reveal only a very small $g_L(E)$ and electrical measurements, which predict orders of magnitude larger $g_L(E)$. A model proposed resolves this conflict by assuming that because of spatial potential fluctuations electrons and holes are trapped in different regions and that near the mobility edge the extended electron wavefunctions are somewhat excluded from regions in which electrons are localized. The consequences of this model regarding the interpretation of the optical and the electrical gap are discussed.

1. Introduction

Studies of the optical absorption and of the electrical conduction have taught us most of what we know about amorphous semiconductors[1]. Their transparency in the infrared spectral region tells us that there exists a gap between valence and conduction bands. The temperature dependence of the electrical conductivity seems to support this picture: the conductivity increases exponentially[2] with temperature as

$$\sigma = \sigma_0 \exp(-\Delta E/kT), \tag{1}$$

similar to the behavior of intrinsic semiconductors. The magnitude of ΔE is roughly ½ of that of the optical gap. This behavior seems to be in accord with the general rule formulated by Yoffe and Regel[3], that it is the short-range order of a material, i.e., the coordination environment of the atoms, which determines whether a material is metallic, semiconducting, or insulating. When there is no long-range order the structures in the optical spectra charac-

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teristic of the translational symmetry of the crystal are absent. Furthermore, the band edges cease to be well defined and one expects the densities of states to tail into the gap, since the gap is a forbidden gap only when there is perfect order. One major difference between crystalline and amorphous semiconductors is their response to impurities. In crystalline semiconductors minute concentrations of foreign atoms acting as donors or acceptors can drastically change their properties, making them strongly n-type or p-type. In contrast, most amorphous semiconductors remain "intrinsic" semiconductors even with additions of a few percent of foreign atoms[4-6]. The cause for this is the possibility and tendency in amorphous materials for foreign atoms of different valency to form their specific coordination environment and hence to satisfy their valence requirements.

Although this picture of an amorphous semiconductor appears to be quite plausible several serious difficulties have become apparent in a number of materials recently. These are the following:

1) According to the optical absorption data the gap contains a small density of localized states, perhaps less than 10^{16} eV^{-1} cm^{-3}, except for regions close to the edge;

2) Electrical measurements appear to reveal a rather large density of states, about 10^{19} eV^{-1} cm^{-3} at the Fermi level which is near the center of the gap;

3) If the ac conductivity of amorphous semiconductors in the radio frequency and microwave range is interpreted[7] as phonon assisted hopping, then a density of states near the Fermi level is obtained which is equal or higher than that suggested by the other electrical measurements;

4) The electron spin resonance signal corresponds to about 2×10^{20} cm^{-3} unpaired and rather localized electrons in amorphous Ge, Si and SiC, whereas in chalcogenide glasses the free spin concentration is many orders of magnitude smaller.

In this paper the conflicting evidence for the density of the localized gap states is critically analyzed. A model is proposed which resolves this conflict by proposing that the regions in which predominantly holes are localized are not the same regions in which electrons are localized. Furthermore, it is suggested that one should distinguish between three kinds of states: (i) states localized in certain regions, (ii) channel states which extend through the material but are excluded from certain regions, and (iii) extended states which describe electrons for which the probability to be found anywhere in the material is finite. This model predicts (a) alternative interpretations of some of the electrical measurements, (b) a very small recombination cross section for localized states near the gap center, and (c) a very small matrix element for optical transitions between localized gap states and extended channel states of type (ii) for photon energies smaller than the optical gap.

2. Optical absorption

The optical absorption constant α of most amorphous semiconductors[1,6] increases exponentially with photon energy in the range of $1 < \alpha < 10^4$ cm^{-1}. As a typical example the absorption curve[9] of As$_2$Se$_3$ is shown in fig. 1. Below α smaller than 1 cm^{-1} the absorption curve changes less rapidly with
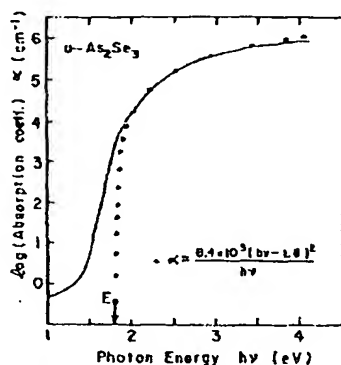

Fig. 1. Absorption coefficient α of amorphous As$_2$Se$_3$ according to Owen and Robertson[9]. The open dots represent a fit of eq. (3) of text to the high energy region.

photon energy. It is uncertain whether this part of the absorption curve truly represents absorption or whether light scattering accounts for the loss of light intensity[10]. At higher photon energies and at α larger than 10^4 cm^{-1} the absorption curve begins to level off. Here the absorption curve has the shape expected for transitions between two bands of states. As suggested by Velický and shown by Tauc et al.[11] the absorption constant can be written as

$$\alpha = \text{const}\, \frac{|M|^2}{h\nu} \int_0^{h\nu - E_0} g_v(E)\, g_c(h\nu - E_0 - E)\, dE, \qquad (2)$$

where the integral is the energy conserving convolution of the density of states $g(E)$. All energy conserving transitions are allowed since there is no crystal momentum to be conserved in the absence of translational symmetry. With the density of states function $g(E)$ proportional to $E^{\frac{1}{2}}$ as in a free electron gas, one obtains

$$\alpha = \text{const}\, \frac{|M|^2}{h\nu}\, (h\nu - E_0)^2. \qquad (3)$$

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Plotting the square root of $h\nu\alpha$ against photon energy should result in a straight line if the matrix element M remains fairly constant in this energy range. This indeed is found in many semiconductors. As an example $(\alpha h\nu)^{\frac{1}{2}}$ of As_2Se_3 is plotted[9] against $h\nu$ in fig. 2. On this plot the exponential absorp-
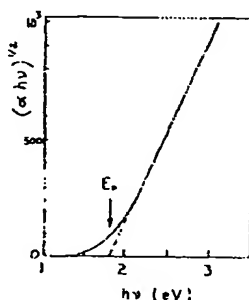

Fig. 2   Dependence of $(\alpha h\nu)^{\frac{1}{2}}$ on photon energy for amorphous As_2Se_3 according to Owen and Robertson[9]. The intercept of the straight line portion with the abscissa defines the optical gap E_0.

tion edge in the range $1 < \alpha < 10^4$ cm^{-1} appears only as a small tail at lower photon energies. The extrapolation of the linear portion of fig. 2 intersects the abscissa at an energy E_0. This value is a convenient fiducial mark to locate the otherwise structureless absorption curve[12]); one refers to it as the *optical gap*.

Evidence for optical transitions from localized gap states to extended band states (or from valence band states to unoccupied localized states above the Fermi level) must be sought at energies near and below E_0. If the matrix element for transitions between localized and extended states is of the same order of magnitude as that for transitions between band states, as shown by Davis and Mott[7]), then the exponential absorption curve of fig. 1 sets an upper limit to the density of localized gap states, for the case shown, α decreases by four orders of magnitudes between 1.8 eV and 1.4 eV. The absence of any significant absorption at lower photon energies implies (with the constant matrix element assumption) that the density of states must remain below about 10^{16} eV^{-1} cm^{-3} throughout the rest of the gap. The density of localized gap states must actually lie significantly below this estimated upper limit because it is very unlikely that the tailing of the localized states is responsible for the exponential part of the absorption edge for the following reasons. Except for amorphous GeTe[15]) and amorphous Ge[14]),

the absorption edge of most amorphous materials[1,8,9]) rises exponentially with the same characteristic slope of about 50 meV. It would be fortuitous if semiconductors having very different compositions and different magnitudes of optical gaps would all have a similar tail of localized gap states. Furthermore, such an exponential absorption tail is observed in many crystalline compound semiconductors[8]) and hence is not a consequence of disorder.

From the optical absorption data we are forced to conclude then that except for small regions near the band edges the density of localized states in the gap must be less than 10^{16} eV^{-1} cm^{-3} if the transitions are governed by matrix elements of the order of those for band to band transitions.

3. Electrical measurements

One consequence of the absence of a large density of states in the forbidden gap in crystalline semiconductors is the ease with which the Fermi level can be shifted into close proximity of the valence band edge or the conduction band edge either by doping the crystal with atoms of different valency or by shifting the surface potential by means of applying a surface charge. In contrast to this the Fermi energy of amorphous semiconductors appears to be very effectively pinned near the center of the gap[15]). Let us review some of the evidence.

Electrical contacts to amorphous semiconductors are usually of low resistance[15]). They do not show the characteristic Schottky barrier layers typical of contacts with crystalline semiconductors. The surface potentials seem to be screened within less than 100 Å. It proves very difficult for instance to swing the surface potential up and down by different adsorbed surface layers or surface charges produced by field effect modulation[16]). Fig. 3 shows schematically what one would expect in a field effect experiment. Shown[16]) here is the change of conductance of $\Delta G/G$ of a film of thickness d as a function of the change of the surface potential from a flat band position for various ratios b of the mobilities of electrons and holes. L is the screening length which is

$$L = \left(\varkappa/4\pi e^2 g\left(E_F\right)\right)^{\frac{1}{2}}, \tag{4}$$

if the density of states at the Fermi level, $g\left(E_F\right)$, is responsible for the screening. Here $\varkappa$ is the dielectric constant. A density of states of about $g(E_F) = 10^{19}$ eV^{-1} cm^{-3} is needed to explain the failure so far of observing the field effect in amorphous Ge and several chalcogenide glasses.

The space charge accompanying the band bending near the surface results in an interface capacitance. The change of this capacitance with bias has been a powerful tool in crystalline semiconductors for determining the

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screening length and thus the density of screening charges[17]. Similar experiments with amorphous semiconductors[18,15] have failed so far. This can be understood if the screening length is very short, i.e., less than 60 Å. This small screening length in turn is a measure of the pinning of the Fermi level and the density of states near the gap center.
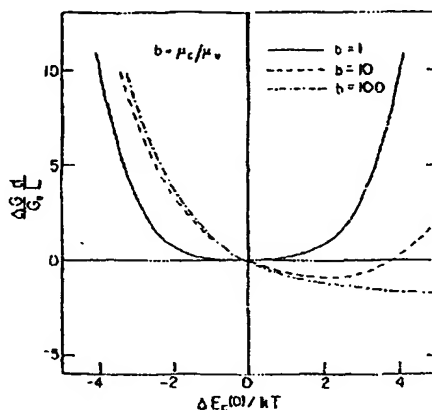

Fig. 3. The relative change of conductance G of a film of thickness d as the potential at the surface is shifted from the flat band position by the amount $\Delta E_F(0)$. L is the characteristic screening length which depends on the density of screening centers. For details see ref. 16.

If the gap were as free of states as the optical measurements indicate, then it should be possible to shift the Fermi level by doping close to either band edge and thus to produce a strongly n-type or p-type material or even a p–n junction. This has never been observed. It appears unsatisfactory to explain this failure by referring to the tendency and possibility of each atom to fulfill its valency requirement. Most preparational methods are such that at least one out of 10^5 atoms should fail to fulfill their valence bonds and give rise to donors and acceptors. It would be fortuitous if donors and acceptors just compensate one another in number or if these states all fall into the center of the gap[7] thereby pinning the Fermi level. The absence of an optical absorption edge at photon energies corresponding to about half the optical gap argues against the presence of a narrow band of localized states near the gap center which was suggested by Davis and Mott[7] to solve the conflict between the electrical and the optical evidence for localized gap states[19].

The examples discussed so far deal with phenomena close to the surface of

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the amorphous semiconductor. Since we cannot exclude the possibility that the Fermi level near the surface is pinned by a large density of surface states we now turn to examples dealing with bulk properties of the semiconductor.

The drift mobility of photoinjected carriers in amorphous semiconductors show that the drift mobility is trap limited[20]. These traps are relatively shallow, of the order of 0.1 eV from the mobility edge. If the number of deep traps and recombination centers near the gap center is appreciable it would seem that a larger number of photoinjected excess carriers should be lost by recombination than is observed. Unfortunately, without values available for the relevant cross sections it is difficult to estimate an upper limit of the density of states near the center of the gap which would be compatible with these experiments[21]).

The slow decay of the photoconductivity of many chalcogenide glasses at liquid nitrogen temperature speaks in favor of the presence of deep traps[22]). The measurement of thermostimulated currents have enabled us to estimate a trap density of about 10^{19} eV^{-1} cm^{-3} near the gap center of a chalcogenide alloy glass[22]). It is unfortunate that not more data are available on thermostimulated currents or thermostimulated depolarization[23]). The few results which are available reveal a density of localized states which is appreciably larger than that deduced from optical absorption measurements.

The ac conductivity of all amorphous semiconductors studied so far[24]) exhibits a dependence on frequency proportional to ω^s where the power s is between 0.7 and 1.0. This power law and the fact that the ac conductivity is almost temperature independent has been used as evidence that the ac conduction is due to phonon assisted hopping of electrons between localized centers near the Fermi level. Austin and Mott[25]) adapted the theory of Pollak and Geballe[26]) to the case of amorphous semiconductors and derived the following expression for the ac conductivity

$$\sigma(\omega) = \tfrac{1}{3}\pi [g(E_F)]^2 kTe^2 a^5 \omega [\ln(v_p/\omega)]^4, \qquad (5)$$

where a is the effective radius of the localized state's wave function and v_p is the phonon frequency. Davis and Mott[7]) plotted the ac conductivity measured at 1.6×10^5 Hz for various materials as shown in fig. 4. The density of states at the Fermi level derived from the expression (4) with the assumption that $a = 8$ Å is indicated on the second abscissa. The absolute magnitude of the density of states obtained is uncertain because of the difficulty of estimating a. The order of magnitude, however, is in accord with the other electrical measurements and in strong disagreement with the optical absorption data as already pointed out by Davis and Mott.

By analyzing their ac conductivity measurements of Se, Lakatos and Abkowitz[24]) find that the large value of $g(E_F)$ they obtain from the hopping model

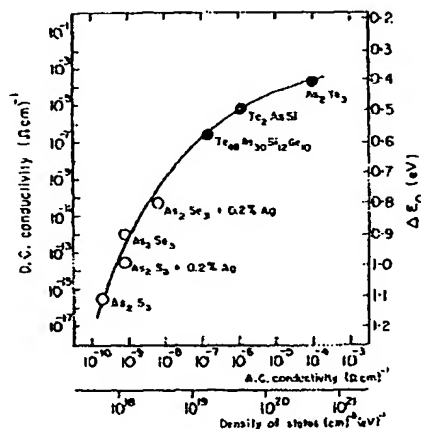56   H. FRITZSCHE

Fig. 4. The relation between dc conductivity, conductivity activation energy ΔE_0, and ac conductivity of several amorphous semiconductors according to Davis and Mott[7]. The density of states $g(E_F)$ is obtained by these authors from eq. (4) of text. The dc conductivity and ΔE_0 are related because the factor σ_0 of eq. (1) is nearly the same for these materials.

and eq. (4) contradicts the evidence obtained from photoinjection measurements that the Fermi level is *not* pinned in amorphous Se.

Since the frequency dependence of the ac conductivity often is used as evidence for the hopping conduction processes of the kind described by Pollak and Geballe one should examine this point in greater detail.

4. AC conductivity

The variation of the conductivity of As_2Se_3 over a large frequency range[27] is shown in fig. 5. The scale on the right hand side shows the product of the refractive index n and the absorption coefficient α. The steep curve above 1.5 eV corresponds to the optical absorption edge discussed in the first section (see fig. 1). Between 1 and 0.1 eV lies the region of transparency which makes this material interesting and useful for infrared lenses and windows. In the frequency range between 10^{12} and 10^{13} Hz some vibrational bands are observed which were recently studied by Taylor, Bishop and Mitchell[21]. At lower frequencies the conductivity increases somewhat less than linearly with frequency. Plotted are the measurements by Ivkin and Kolomiets[28] and by Owen and Robertson[9]. The latter authors used As_2Se_3 contaminated with 0.2 at% Ag and found an ω^2 dependence of the conductivity between

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10^6 and 10^8 Hz. At low frequencies the conductivity is constant and equal
to the dc conductivity. The ac conductivity at higher frequencies is nearly
temperature independent whereas the dc conductivity follows eq. (1). The
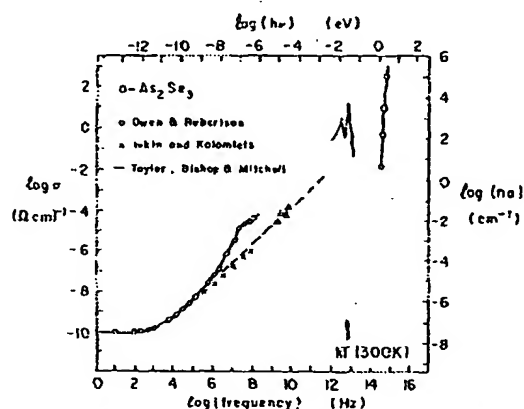$\sigma_{ac} \sim \omega^2$ regime was tentatively associated by Mott[29] with optical transitions

Fig. 5. The ac conductivity of amorphous As_2Se_3 over a wide frequency range. The
right hand scale shows the product of refractive index n and absorption coefficient α.
The dashed line represents an $\omega^{0.9}$ dependence. Data above $h\nu \sim 1$ eV and open circles
are by Owen and Robertson, crosses by Ivkin and Kolomiets, and microwave and infrared
data are by Taylor et al.[37].

between localized states. The presence of this regime, however, is experiment-
ally not well established. It appears to depend on contact properties, sample
purity, and preparation conditions as will be discussed further below.

We wish to emphasize here that σ_{ac} increasing with frequency somewhat
less than linearly is a very common feature of many solid dielectrics, glasses,
ceramics, and plastics. Expressing this fact in terms of the power factor
$\tan \delta = 4\pi\sigma/\omega\kappa$, Gevers and DuPre[30] found for amorphous dielectrics the
following general properties:

(a) The real part of the complex dielectric constant decreases only slightly
with increasing frequency;

(b) The power factor $\tan \delta$ is almost independent of frequency, generally
decreasing gradually with increasing frequency.

Also the magnitude of the ac loss of many amorphous semiconductors is
about the same as that of alkali glasses, porcelain, plexiglass, marble, pyrex,
celluloid, bakelite, and many other non-crystalline materials.

In his review of dielectric relaxation in glasses Owen[31] pointed out that

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an almost constant power factor, which slowly decreases with increasing frequency, is to be expected quite generally whenever there is a wide and flat statistical distribution of relaxation times. Many relaxation processes have been considered by different authors and for each relaxation process one can suppose that the spectrum of relaxation times is rather wide and flat in amorphous materials. The electron hopping process between localized states considered by Mott and Pollak is only one of many possible relaxation processes. Granted that for the hopping mechanism, the spread of the distribution of relaxation times is amplified because they are proportional to an exponential function of a random variable, namely the separation between localized states, it is nevertheless difficult to see why very different noncrystalline dielectrics and semiconductors behave in such similar manner. One is led to conclude that the frequency dependence of the ac conductivity, being a common property of many loss mechanisms, cannot be used to single out the hopping mechanism. The very large density of states at the Fermi level needed by the hopping theory to explain the experimental results appears to argue against electronic hopping in the manner treated by the theory as a plausible explanation.

Careful measurements by Crevecoeur and De Wit of the Philips Research Laboratories indicate that the measurements shown in fig. 5 between 10^2 and 10^9 Hz may not represent losses in bulk As_2Se_3. In fig. 6 Crevecoeur and
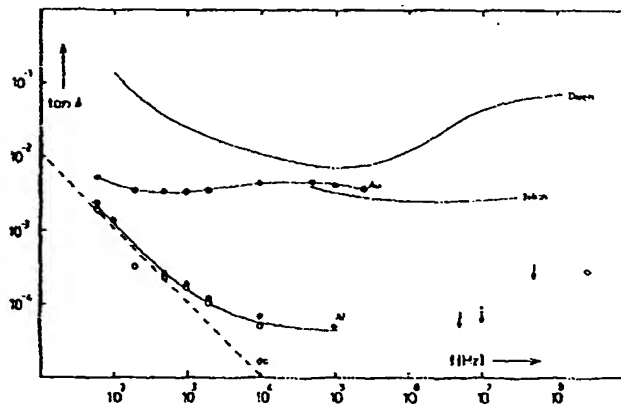

Fig. 6.   Power factor tan δ as a function of frequency of As_2Se_3 according to Crevecoeur and De Wit of Philips Research Laboratories. The data labelled Owen and Ivkin, respectively, are those shown in fig. 5. Au and Al represent electrode material. The arrows indicate that the loss lies below the experimental limits indicated.

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De Wit[32]) plot the results of Owen et al. and Ivkin et al. together with some of their recent results measured at room temperature. The dotted line represents $\tan \delta$ calculated from the dc conductivity $\sigma = 5 \times 10^{-13}$ ohm^{-1} cm^{-1}. It should be noted that Owen et al.[9]) who used As$_2$Se$_3$ doped with 0.2% Ag find also a higher dc conductivity of $\sigma = 10^{-10}$ ohm^{-1} cm^{-1}. Open circles represent measurements on a sample 1 mm thick pressed between copper plates which are used as contacts. Measurements on samples with different thicknesses show that these losses are independent of thickness. The full circles represent measurements on 1 mm thick samples provided with sputtered gold contacts. Evaporated indium contacts cause even larger losses than Au contacts according to Crevecoeur and De Wit. The open triangles represent measurements using evaporated aluminum contacts on a thick sample. In the region of 10^6-10^9 Hz these authors find the losses to be smaller than 10^{-4} (indicated by arrows) which is below the limit of detection of their apparatus. In this last case the samples had no contacts. Crevecoeur and De Wit mention that the low loss values may be influenced by surface and impurity effects and might still not represent the true loss of As$_2$Se$_3$ glass. Evidently not only the quality of the contacts but also that of the samples is of great importance. Similarly careful investigations on other semiconductor glasses are still missing.

We conclude from the foregoing that presently there is insufficient evidence for deducing a large $g(E_V)$ from the ac conductivity in amorphous semiconductors.

5. Electron spin resonance

About 2×10^{20} cm^{-3} of free spins have been observed at liquid nitrogen temperatures in amorphous Ge, Si and SiC[27]. It was reported[33]) that the number of free spins increases with the thickness of the samples and hence scales with the volume of the material. This spin signal has been observed in evaporated and sputtered films, not however in Si films prepared by means of a high frequency gas discharge from silane[34]). It is generally believed that these spins are associated with surface states at internal surfaces of cavities or voids in the amorphous film[35]). Their number decreases drastically as the material is annealed at higher temperatures.

In contrast to these observations we have found[36]) a very small spin resonance signal in chalcogenide glasses prepared by quenching from the melt. The spin density here is of the order of 10^{15} or 10^{16} cm^{-3} and depends on the thermal history of the sample. In many samples including As$_2$Se$_3$, As$_2$S$_3$, and Se no signal could be detected with a sensitivity of 10^{14} cm^{-3}. No spin signal has been observed by us in sputtered or evaporated chalcogenide films with a detection sensitivity of 10^{17} cm^{-3}. Illuminating the samples at liquid

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nitrogen temperature with electron hole pair producing light, thereby disturbing the equilibrium distribution of the charge carriers, did not produce a measurable ESR signal. Samples which did not show an ESR signal at liquid nitrogen temperatures were cooled to 1.5 K. In no case was a signal observed with or without illumination.

The absence of an ESR signal may be caused by short relaxation times and hence does not preclude the presence of spin states. Tauc et al.[16] measured the magnetic susceptibility of very pure amorphous As_2S_3 and obtained from the Curie term a spin density of 6×10^{17} cm^{-3}. Equating this density with the total concentration of occupied and localized valence band states these authors fit the weak absorption region ($\alpha < 1$ cm^{-1}) to an exponential tail of localized states and deduce that the optical matrix element for transitions between localized and band states must be many orders of magnitude smaller than that between extended states of different bands.

We conclude from these experiments the following: The spin density in amorphous Si, Ge, and SiC is too large to be associated with localized gap states[37]. The rather large Curie term found in As_2S_3 signifies an appreciable total density of localized gap states since only a fraction of these can have unpaired spins[37].

6. The model

The main conflict of the magnitude of the density of gap states is between the evidence obtained from optical absorption on the one hand and from electrical measurements on the other. The main conflict of the magnitude of the density of gap states is between the evidence obtained from the optical absorption on the one hand and from electrical measurements on the other. A large density of localized gap states can exist without being detectable by optical absorption if the matrix element for optical transitions between localized and extended states is much less than that between extended states of different bands. One important difference between optical and electrical measurements lies in the fact that optical absorption is rather insensitive to potential fluctuations whereas for electrical measurements these are of great importance. The situation is similar to the case of a p-n junction in a crystalline semiconductor. The junction is not noticeable optically (except for a small influence of the electric field on the absorption process within the junction) but its effect on the conduction properties is unquestionably strong.

By the procedure illustrated in fig. 2 the optical absorption curve yields the optical gap E_0. We use this optical gap in fig. 7 to illustrate schematically the long wavelength potential fluctuations in an amorphous material. The longest wavelength is limited by the screening length. The shortest wavelength chosen is sufficiently long to smoothen out the local potential and the short

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range wiggles of the wave function. It should be noted that the lines drawn do *not* represent a valence band edge or conduction band edge nor do they represent the true local potential felt by charge carriers. It might be more correct to think of the local potential averaged over a region of order the
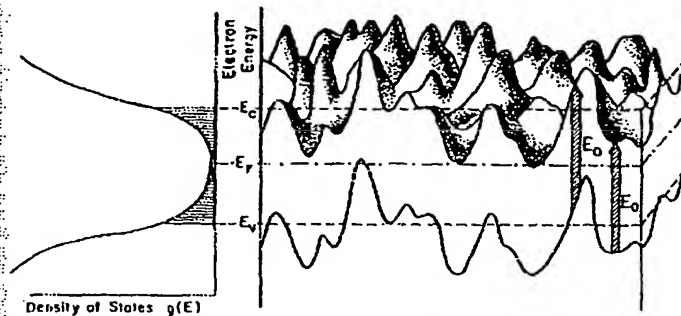

Fig. 7.   Potential fluctuations of the initial and final electron states for the optical transitions corresponding to the optical gap E_0. The left hand side shows the density of states. The region of localized states lies between E_c and E_v. Note that the short range potential wells which give rise to many of the localized states are not shown here. This figure shows only that part of the long wavelength potential fluctuations which cause a parallel shift of the valence and conduction band states. The part which causes a spatial variation of E_0 is omitted for clarity.

coherence length of the electron taking part in the optical transition. The two vertical arrows represent optical transitions of energy E_0. Local density fluctuations or compositional variations are expected to produce spatial variations of E_0. These were illustrated by Heywang and Haberland[38]) and are omitted here for clarity and should be thought of as being included. In other words E_0 as obtained from the absorption data is itself an average over different regions. Fig. 7 illustrates that optical transitions are insensitive to potential fluctuations. They are affected only by the local electric field. These fluctuations can however very effectively pin the Fermi level near the center of the gap. Although the electron energy levels have to be calculated self-consistently with the potential fluctuations present, it appears plausible to draw a density of states curve as shown on the left hand side of fig. 7. Most of the localized gap states are thought of originating from potential fluctuations which are of much smaller scale than the short wavelength limit and therefore not shown on the right hand side of fig. 7.

Let us now inquire which states are likely to be localized and which can provide conduction from one side of the amorphous semiconductor to the other. Again we use fig. 7 as a schematic and not as a true representation of

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the local potential. As indicated by the work of Cohen[29] and Cohen et al.[40]), from a classical point of view this is a percolation problem. For energies $E < E_c$ an electron is localized, i.e., confined, to a certain region L. The rest of the material is prohibited (P) for the electron, which means that the wave function falls off rather rapidly with distance away from region L. Percolation theory predicts that at a certain energy E_c the probability for finding a path A for an allowed region extending throughout the material becomes finite. The probability then increases very rapidly with E above E_c. Fig. 8
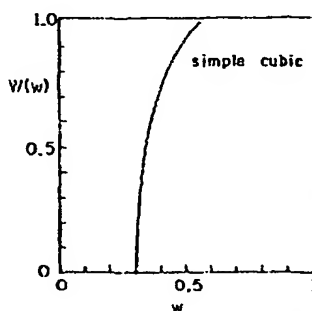

Fig. 8. The probability of finding a connected path in a simple cubic lattice as a function of the probability of bond occupation.

shows the result of a Monte Carlo calculation[41]) of the probability W for finding a continuous path through a simple cubic lattice whose interconnecting bonds are occupied with the probability w. Using instead of w the space occupation of allowed bonds one defines the critical percolation density ρ_c. This value is about $\rho_c = 0.15$ for all three dimensional lattices[43]) and is therefore expected to be similar for a random network lattice. Fig. 9 shows schematically[39]) the isolated allowed regions L for $E < E_c$, the coexistence of a continuous path A and islands for $E \gtrsim E_c$, and finally the shrinkage of prohibited volumes P as $E \gg E_c$. The same arguments hold for holes for which one can define a critical percolation energy E_v.

As mentioned above the steep and narrow potentials fluctuations which give rise to localized states are not shown in fig. 7. Their height is modulated by the long wavelength potential fluctuations shown. It is of importance to note that in this model the electrons are localized predominantly where there are no holes and most holes are localized at places different from the electrons. The critical energies E_c and E_v are common to the whole material as is the Fermi energy and undergo no spatial fluctuations.

An extended state does not necessarily extend everywhere. The first ex-

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tended states close to E_c and E_v are channeling states, occupy a small fraction of space, and coexist in this classical picture with many localized regions. As soon as we allow tunneling to occur, these localized regions cease to be localized and give rise to resonance states. Only for energies further into the
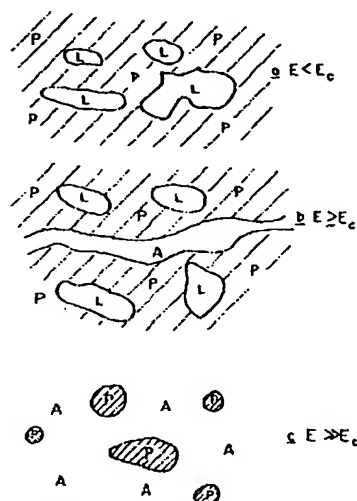

Fig. 9. (a) For energy below the percolation threshold E_c one finds localized allowed regions L imbedded in prohibited space P. (b) When $E = E_c$ the first allowed paths A connect one side of the material with the other. They coexist with allowed islands L. (c) At high energies $E \gg E_c$ the prohibited regions have shrunk to isolated islands.

bands can we talk of extended states in the more general sense. Fig. 10 shows the density of states corresponding to the localized regions and of the extended states. The same figure shows the mobility at $T=0$ decreasing to zero for energies between E_c and E_v where there are no extended states. This defines the mobility gap in the CFO model.[43] As mentioned by Cohen[39] the mobility near E_c and E_v will smoothly go to zero because of the resonance effects which result from the coexistence of extended channel states and "localized" states. At finite temperatures thermally activated hopping smears out the mobility edge as shown in the upper sketch of fig. 10.

Since the long wavelength limit of the potential fluctuations is about the size of the screening length, it is possible that the allowed regions shown in fig. 9 for $E < E_c$ extend over, say 150 Å and contain a number of localized

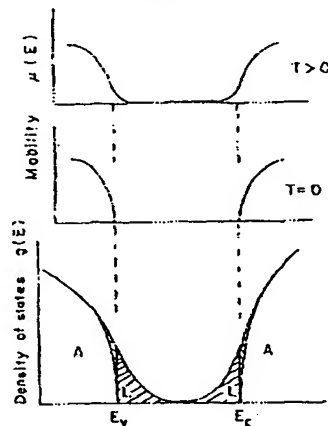64   H. FRITZSCHE

Fig. 10. The lower half shows the density of states $g(E)$ as a function of electron energy. Localized states and regions are found between the percolation thresholds E_a and E_x. They coexist in this classical picture with extended channel states for some energy beyond E_c and E_v. At absolute zero one expects mobility edges at E_c and E_v which become less sharp at finite temperatures where phonon assisted hopping can occur between localized regions and states.

states. Many of these may themselves be contained by individual potential wells since fig. 7 does not show the real local potential.

This model resolves the conflict between the optical and electrical measurements with regards to the density of gap states. The fact that the localized gap states are not discernable optically is here attributed to the fact that the extended conduction band states of lowest energy are channel states which are essentially excluded from the regions where electrons are localized. The extended electron states whose wavefunctions have appreciable magnitude everywhere in the material are found only at higher energies. This can be expressed in terms of a rapidly decreasing matrix element for optical transitions between localized states and nonlocalized states as the photon energy is decreased below the optical gap. At the same time this model allows for the possibility that the Fermi level is quite effectively pinned near the center of the mobility gap. In addition, recombination processes are greatly inhibited once the charge carriers are trapped because the traps for electrons are not at the same places as the traps for holes. This is in accordance with the slow decay time of the photoconductivity at low temperatures. Furthermore, in Se it has been noted [44] that a space charge of trapped electrons can be compen-

ated by a space charge of trapped holes without achieving a significant re-combination between these two opposite charges. When the local distance between states of opposite charge is large one expects what Weiser et al.[45] have noticed in 2 $As_2Te_3 \cdot As_2Se_3$ that recombination practically does not take place through states in the neighborhood of the gap center.

On the basis of this heterogeneous model one can explain a low contact resistance without demanding that a Schottky barrier be absent or so narrow that tunneling through it can easily take place. If the surface potential at the contact interface varies as much as the potential inside then a sufficient number of spots are open for charge carriers to enter without overcoming a potential barrier.

It might be necessary to reevaluate the expression for ac hopping conduction to allow for the possibility of hopping between localized regions in addition to localized states.

7. Electrical energy gap

The optical gap E_0 is often compared with ΔE, the activation energy calculated from an Arrhenius plot of the conductivity as expressed in eq. (1). The difference between E_0 and $E_g = 2\Delta E$ is often interpreted as an activation energy of the mobility. Let us investigate what quantity actually is measured by the Arrhenius plot and whether it bears any relationship with the optical gap E_0.

Although the current will be carried by both electrons and holes, it is likely that one kind of carrier contributes a larger share to the conductivity. As an example let us assume that the holes are the dominant charge carriers. The energy of eq. (1) is then

$$\Delta E = E_F - E_v. \tag{6}$$

This differs from the expression for an intrinsic semiconductor for which one would expect

$$\Delta E = \tfrac{1}{2}(E_c - E_v), \tag{7}$$

because in the amorphous semiconductors we assume that the position of the Fermi level is fixed by the neutrality condition including the charges on the localized states and not be equating the concentration of free electrons and free holes as in the case of intrinsic semiconductors.

The energy ΔE will depend on temperature. $\Delta E(T)$ probably has the shape as shown in fig. 11. The curve approaches $T=0$ with zero slope and $\Delta E(T)$ is expected to decrease with increasing temperature because of the increased number of phonons similar to the temperature dependence of the optical gap in amorphous semiconductors[46] and band gaps in crystalline semiconductors. Above the Debye temperature $\Delta E(T)$ will decrease almost linearly with

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temperature so that we can approximately write for the higher temperatures

$$\Delta E(T) = \Delta E_0 - \beta T. \qquad (8)$$

There may be higher order terms in temperature but these are neglected when a constant ΔE is determined from the slope of the conductivity curve in a given temperature interval. Fitting the conductivity in a certain T-range with eq. (1) is tantamount with approximating the true $\Delta E(T)$ curve with the
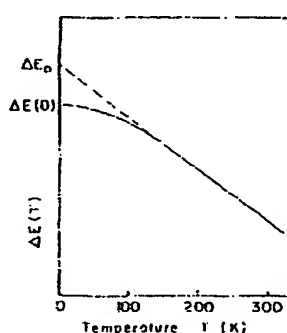

Fig. 11.   The expected temperature dependence of $\Delta E = E_F - E_v$ or of $E_c - E_F$. From the slope of an Arrhenius plot of the conductivity one obtains ΔE_0 and not $\Delta E(0)$.

linear approximation of eq. (7). Substituting eq. (7) into eq. (1) one obtains

$$\sigma = \sigma_0 \exp(\beta/k) \exp(-\Delta E_0/kT). \qquad (9)$$

Hence the slope of the Arrhenius plot yields ΔE_0, the $T=0$ intercept of the tangent to $\Delta E(T)$ in the measured temperature range. ΔE_0 lies appreciably higher than the $T=0$ value of $\Delta E(T)$. The temperature coefficient β contributes a constant prefactor to the exponential of eq. (1). It is possible to obtain β from thermopower measurements[7]. Since it is unlikely that the Fermi level lies exactly between E_c and E_v, one cannot obtain $E_c - E_v$ from ΔE_0. From the previous discussion it is apparent that the optical gap E_0 bears no direct relationship with ΔE_0. The optical gap can be somewhat larger or somewhat smaller than $2\Delta E_0$ depending on the magnitude of the potential fluctuations and the position of E_F relative to the critical percolation energies and no information can be obtained from this difference about a possible activation energy of the mobility. The pressure coefficient of the optical gap and of the value ΔE_0 has been measured[46] for two chalcogenide alloy glasses. In both cases the pressure coefficients differed by almost a factor of two in agreement with our notion that these two quantities are actually unrelated.

8. Internal potential fluctuations

Although the existence of internal fields has been assumed by almost every theorist dealing with amorphous materials[47]) their magnitude or origin is still quite unclear. They are likely to have quite different character in elemental amorphous materials and in alloy glasses which allow compositional disorder. Potential fluctuations which affect both valence and conduction states in the same manner are associated with charged centers or regions which in turn may be related to impurities and structural disorder.

In contrast to crystalline semiconductors whose rather narrow solubility limits restrict the concentration of impurities, particularly those giving rise to deep gap levels, amorphous semiconductors probably contain a rather high density of uncontrolled and unknown impurities. Since the electrical properties of amorphous semiconductors are so much less sensitive to impurities compared to those of their crystalline counterparts, relatively little attention has been paid to holding down the contamination level. Although a good fraction of these impurities will satisfy their valence bonds by choosing their favorite coordination environment, a sufficient number might fail to do so, giving rise to internal fields and spatial potential fluctuations.

Even without invoking impurities and dangling bonds, charge and potential variations are expected to result from variations in electronegativity which in turn are a consequence of spatial fluctuations in structure, density, and composition. Furthermore, the large difference in electronegativity between the first row elements C, N, and O and the heavier elements in the respective columns of the periodic table may cause a local charge transfer when isoelectronic elements are interchanged even without a change in the coordination environment. In crystalline materials this electronegativity difference is the origin for the isoelectronic donor centers[48]).

Recently, M. Pollak discussed a different cause for the presence of charged centers[49]). Consider a localized valence bond state V (occupied and hence neutral) and a localized conduction bond state C (unoccupied and therefore neutral), being moved together. One has to imagine the structural environment which gives rise to these localized states to be moved along. At large distances the energy difference $E_i - E_a$ between the ionization energy of V and the electron affinity of C is required to form the ionic pair V^+C^-. As soon as the Coulomb energy of V^+C^- exceeds $E_i - E_a$ at small distances, the ionic pair is energetically favored. This rough model of the formation of an ionic diatomic molecule has to be amended naturally to include screening and the interaction of the structural environments which gives rise to these localized states. It illustrates, however, the importance of Coulomb effects in the self-consistent treatment of the localized states.

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9. Summary and conclusions

The presence of potential fluctuations in amorphous semiconductors might explain the absence of transitions between localized and extended states in optical absorption at photon energies below the optical gap and, at the same time, the rather effective pinning of the Fermi energy observed in electrical transport experiments in many amorphous semiconductors.

Mott[59] estimates for chalcogenide glasses a density of states $g(E_c) \approx 10^{21}$ $cm^{-3} eV^{-1}$ at E_c and a range of localized states of order $\Delta E \sim 0.1$ eV. With $g(E)$ falling off linearly, this estimate yields a density of about $10^{20} cm^{-3}$ localized states associated with both bands. It is proposed here that potential fluctuations can spread the range of localized states sufficiently to reach the center of the gap from both the valence band and the conduction band side and to yield the pinning of the Fermi level observed in many amorphous semiconductors. It is then not necessary to assume a peak in the density of localized states near the center of the gap as suggested by Davis and Mott[7]. The wavefunction of extended states near E_c and E_v is expected to be small where the long wavelength potential fluctuations exclude electrons or holes, respectively.

The effect of the potential fluctuations causes only a broadening of the absorption edge through the electric field assisted absorption. Their effect on the transport phenomena is much more profound. They tend to divide the material into regions of electron traps and regions of hole traps. As a consequence, localized states near the middle of the gap do not act as efficient recombination centers.

The heterogeneity of the current flow near the mobility edges predicted by the model proposed requires modifications in the interpretation of several contact, interface and transport phenomena, particularly the Hall effect, magnetoresistance, and ac conductivity. According to this model a charge can be conducted along paths near the percolation threshold without surmounting potential peaks. The energy separation $E_c - E_v$ between the mobility edges for electrons and for holes bears no immediate relation with the optical gap E_0. The slope of the Arrhenius plot of the resistivity yields a quantity ΔE_0 from which one may obtain the distance of the Fermi energy from the mobility edge of predominant conduction. The optical gap E_0 may be larger or smaller than the quantity $2\Delta E_0$. It does not seem possible to obtain an activation energy of the mobility from a comparison of these two quantities.

The interpretation of experiments predicting large densities of localized gap states is far from unambiguous. A high density of surface states may account for part of the field screening at the semiconductor surface or interface and relaxation processes other than hopping conduction between pairs

of localized states may be responsible for the increase of the ac conductivity with frequency. It appears that more attention to impurity and contact effects is warranted and that very few experiments have been carried out from which the density of gap states can be determined.

It would be inappropriate to apply this model, which describes certain consequences of long wavelength potential fluctuations, to all amorphous semiconductors. In some classes of materials, such as the transition metal-oxide glasses these potential fluctuations are probably unimportant. Other materials appear to fall into groups with common features which may be associated with specific defect structures which give rise to localized states falling into narrow energy ranges. In particular amorphous films of silicon-oxide and aluminumoxide are quite different from the amorphous tetra-hedrally coordinated films of Si, Ge and the III–V compounds. Furthermore, the wide bandgap chalcogenide glasses have common features which are different from those of the small bandgap materials. We feel that potential fluctuations play an important role in the chalcogenide alloy glasses which have variations in composition in addition to structural disorder.

It appears important to point out that the potential fluctuations depend selfconsistently on the occupation of the localized states. The position of the critical energies E_c and E_v will therefore be changed with the electron distri-bution at high injection or photo excitation levels or directly by high electric fields. This will affect the high field conduction properties and the phenom-ena associated with electric breakdown[51]).

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